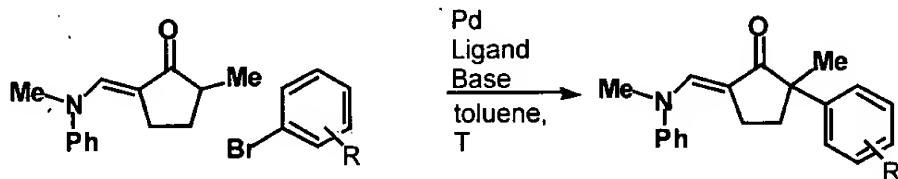


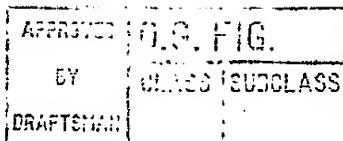
**Figure 1**

Examples of the Asymmetric Arylation of 2-Methylcyclopentanone Bearing a Blocking Group at the 5-Position



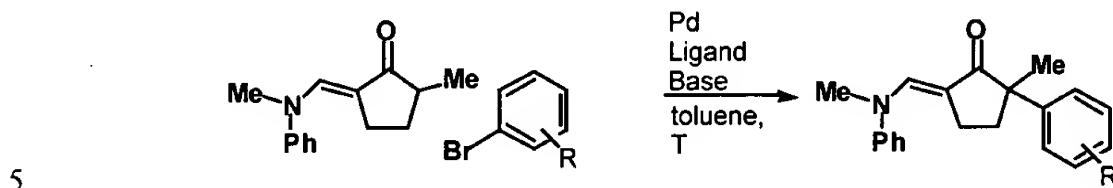
R	Ligand	%Pd	%L	Base	T C°	Y%	ee %
4- <i>t</i> Bu	(S)-BINAP	10	15	NaHMDS	100	67	90
4- <i>t</i> Bu	(S)-BINAP	10	15	NaO <i>t</i> Bu	100	70	89
4- <i>t</i> Bu	(R)-QUINAP	5	7.5	NaO <i>t</i> Bu	90	67	23
4- <i>t</i> Bu	(R)-MOP	10	15	KO <i>t</i> Bu	100	68	34
4- <i>t</i> Bu	(S)-BINAP	10	15	KO <i>t</i> Bu	100	54	84
4- <i>t</i> Bu	(R)-QUINAP	10	15	KO <i>t</i> Bu	100	23	15
4- <i>t</i> Bu	(S)-BINAP	10	15	KO <i>t</i> Bu	100	63	85
4- <i>t</i> Bu	(S)-BINAP	10	15	KHMDS	100	51	86
4- <i>t</i> Bu	(-)1	5	7.5	NaO <i>t</i> Bu	rt	93	68
4- <i>t</i> Bu	(-)1	5	7.5	NaO <i>t</i> Bu	rt	99	67
3-OMe	(S)-BINAP	10	15	NaO <i>t</i> Bu	100	91	85
4-OMe	(S)-BINAP	5	10	NaO <i>t</i> Bu	100	55	62
4-OMe	(S)-BINAP	10	15	NaO <i>t</i> Bu	100	65	57
3-(2-dioxolane)	(S)-BINAP	10	15	NaO <i>t</i> Bu	100	96	86

[1 = 2-(dicyclohexylphosphino)-2'-(dimethylamino)-1,1'-binaphthyl]



**Figure 2**

Additional Examples of the Asymmetric Arylation of 2-Methylcyclopentanone Bearing a Blocking Group at the 5-Position



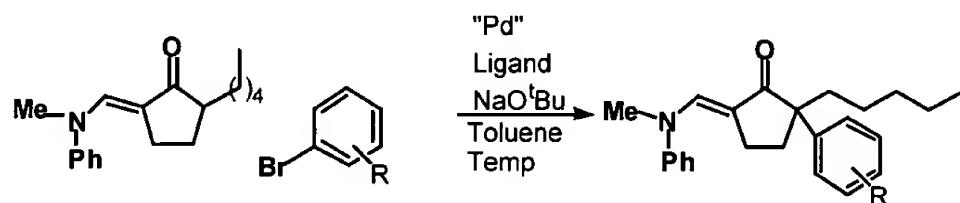
R	Ligand	%Pd	%L	Base	T C°	Y%	ee %
4-Me	(S)-BINAP	10	15	NaO <i>t</i> Bu	100	65	63
4-Me	(R)-QUINAP	10	15	NaO <i>t</i> Bu	100	82	25
4-Me	(-)-1	5	7.5	NaO <i>t</i> Bu	rt	88	75
2-Me	(S)-BINAP	5	10	NaO <i>t</i> Bu	100	52	10
2-Me	(S)-BINAP	5	10	NaO <i>t</i> Bu	100	48	8
3-Me	(S)-BINAP	5	10	NaO <i>t</i> Bu	100	70	80
3-Me	(S)-BINAP	5	10	NaO <i>t</i> Bu	100	72	80
4-CF <sub>3</sub>	(S)-BINAP	10	15	NaO <i>t</i> Bu	100	93	53
4-CF <sub>3</sub>	(S)-BINAP	10	15	NaO <i>t</i> Bu	80	80	44
4-CF <sub>3</sub>	(R)-QUINAP	5	7.5	NaO <i>t</i> Bu	90	54	43
3-CF <sub>3</sub>	(S)-BINAP	5	7.5	NaO <i>t</i> Bu	100	60	75
4-CN	(-)-1	5	7.5	NaO <i>t</i> Bu	rt	51	80

[1 = 2-(dicyclohexylphosphino)-2'-(dimethylamino)-1,1'-binaphthyl]

**Figure 3**

Asymmetric Arylation of 2-pentylcyclopentanone Bearing a Blocking Group at the 5-Position

5

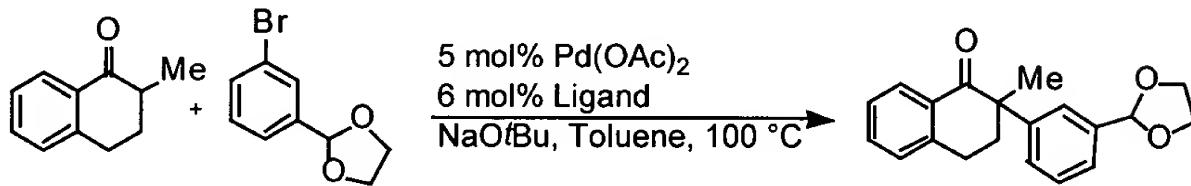


R	"Pd"	Ligand	%Pd	%L	T C°	Y%	ee %
H	Pd <sub>2</sub> (dba) <sub>3</sub>	(S)-BINAP	10	15	93	84	93
H	Pd(OAc) <sub>2</sub>	(-)1	10	15	72	78	72
3-Me	Pd(OAc) <sub>2</sub>	(S)-BINAP	10	15	100	70	99
4-CF <sub>3</sub>	Pd <sub>2</sub> (dba) <sub>3</sub>	(S)-BINAP	10	15	100	71	90

10

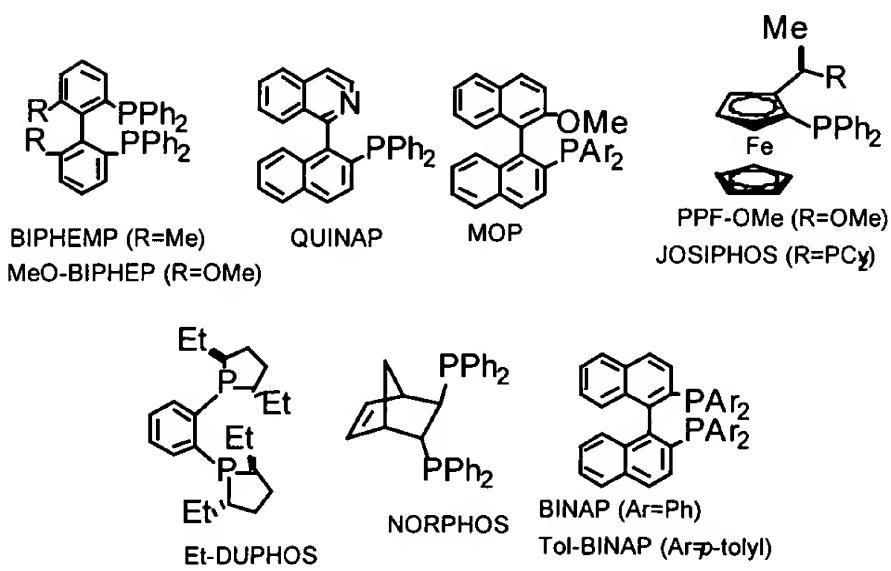
[1 = 2-(dicyclohexylphosphino)-2'-(dimethylamino)-1,1'-binaphthyl]

**Figure 4**  $\alpha$ -Arylation of 2-Methyl-1-Tetralone—Ligand Effects



Ligand	Yield	ee
(S)-BINAP	69	84
(R)-QUINAP	43	84
(R)-MeO-BIPHEP	59	85
(S)-BIPHEMP	39	82
(R,R)-NORPHOS	38	40
(R)-MOP	19	8
(R)-PPF-OMe	38	1
(R)-(S)-JOSIPHOS	38	2
(S)-Et-DUPHOS <sup>a</sup>	8	12
(S)-Tol-BINAP <sup>b</sup>	26	30

(a) Reaction run with 10 mol%  $Pd(dba)_3$ , 24 mol% (S)-Tol-BINAP, NaHMDS as base. (b) Reaction run with 2.5 mol%  $Pd(dba)_3$ , 6 mol% (S)-Et-DUPHOS, NaHMDS as base.



**Figure 5.**  $\alpha$ -Arylations of Ketones in the Absence of a Phosphine Ligand.

entry	Ketone	Aryl Bromide	Pd Source (mol %)	(% yield)
1			$\text{Pd}(\text{OAc})_2$ or $\text{Pd}_2(\text{DBA})_3$ $\text{NaO}^-\text{Bu}$ toluene 80 °C	55%
2			$\text{Pd}_2(\text{DBA})_3$ (1.5 mol %)	54%
3			$\text{Pd}(\text{OAc})_2$ (1 mol %)	79%
4			$\text{Pd}_2(\text{DBA})_3$ (1.5 mol %)	46%
5			$\text{Pd}_2(\text{DBA})_3$ (1.5 mol %)	48%
6			$\text{Pd}(\text{OAc})_2$ (1 mol %)	71%
7			$\text{Pd}(\text{OAc})_2$ (1 mol %)	79%
8			$\text{Pd}(\text{OAc})_2$ (1 mol %)	83%
9			$\text{Pd}_2(\text{DBA})_3$ (0.5 mol %)	79%
10			$\text{Pd}(\text{OAc})_2$ (1.0 mol %)	64%